CONSORTIUM FOR LEAD BATTERY LEADERSHIP

Red Team 2: Failure Analysis and Modeling

Mohammed Effat,[1] Kevin Knehr,[1] Tim Fister,[1] Matthew Nisbet,[1] Tiffany Kinnibrugh,[2]
Matthew Spence,[3] Julian Kosacki,[3] Maureen Kalupa,[3] Matthew Raiford,[4] Alyssa McQuilling,[4] Courtney Greco,[5] Roger Miksad,[5] Tim Ellis[5]
1. Chemical Sciences and Engineering Division, Argonne National Laboratory, 2. X-ray Science Division, Argonne National Laboratory, 3. Clarios, LLC, 4. Consortium for Battery Innovation, 5. Battery Council International

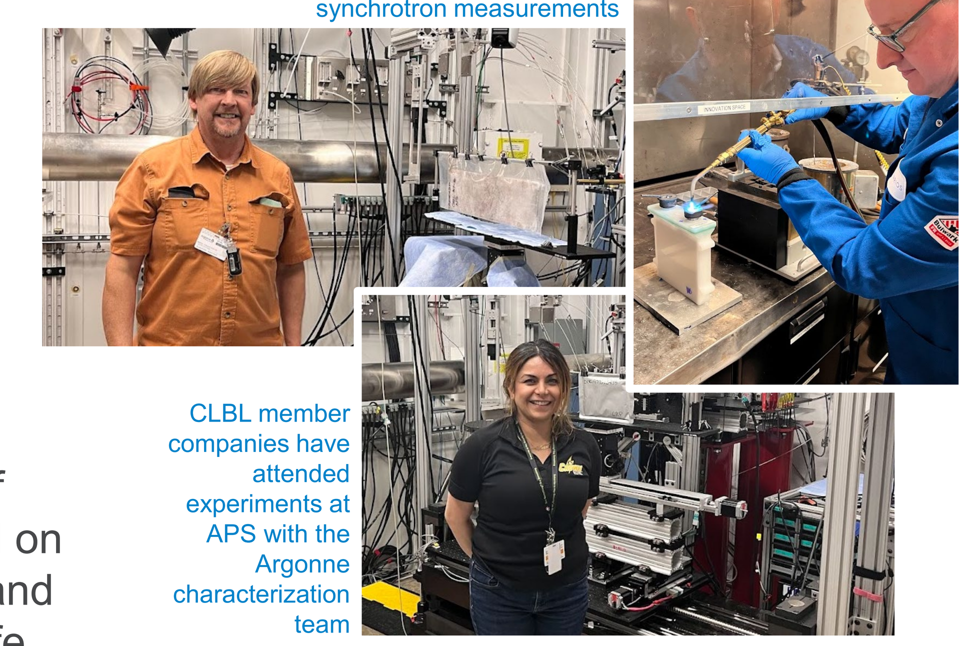
PROJECT PROFILE

Topic: Zinc and Lead Batteries | Vertical: Analytics
Strategic Pathway: Grow Grid Capacity, stabilize grid services
Project start and finish: FY2025 – FY2027

MOTIVATION

Lead acid batteries have a robust domestic supply chain but have largely been developed for automotive or emergency backup applications. This project aims to adapt lead batteries to the durations needed for stationary storage.

Consortium for Lead Battery Leadership (CLBL) combines the background of eight U.S. battery companies with capabilities of DOE national labs. Red Team 2 is focused on understanding markers for battery failure and developing cycling protocols that extend life.



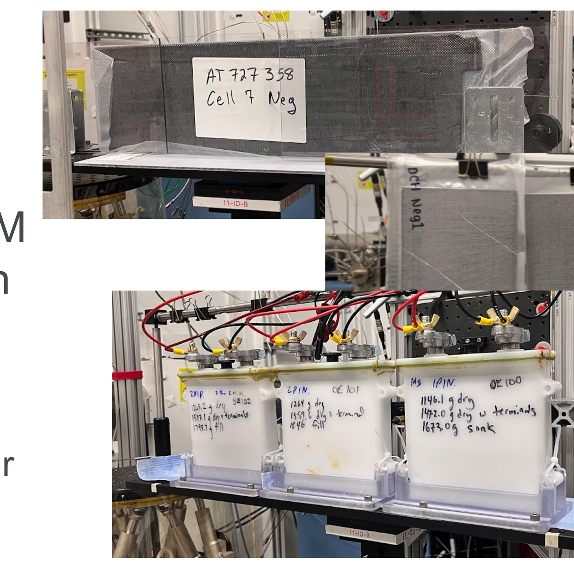
Argonne researchers collaborate with Clarios R&D to develop 2V AGM cells used for operando synchrotron measurements

CLBL member companies have attended experiments at APS with the Argonne characterization team

APPROACH

Experimental Approach: High energy synchrotron x-ray diffraction: correlating changes in speciation and crystal structure with cycling. To date we have measured >13M XRD patterns from >500 electrodes and 16 in situ cells.

- Ex situ electrodes: vacuumed sealed from partner labs and manufacturers and shipped to Argonne.
- In situ 2V cells: 2-3 plate flooded, AGM, and bipolar cells – can measure local charge and currents during cycling, and repeatedly over cell lifetime.

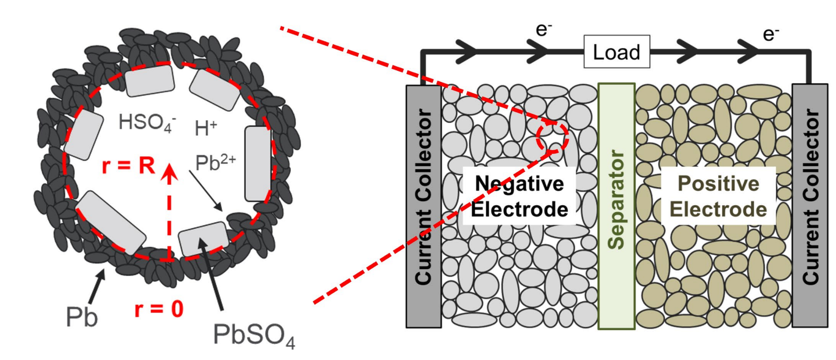


Ex situ studies range from 140 Ah traction batteries to 10 Ah SLI plates

In situ cells include VRLA, flooded, and bipolar variants

Modeling Approach: continuum "Newman" modeling connecting local electrode/electrolyte speciation with electrochemical response. Open questions for CLBL test protocol development:

- *Discharge*: what are limits of utilization? How does this change with electrode dimensions and rate?
- *Charge*: what is optimal charging voltage, overcharge%, and recharge rate?

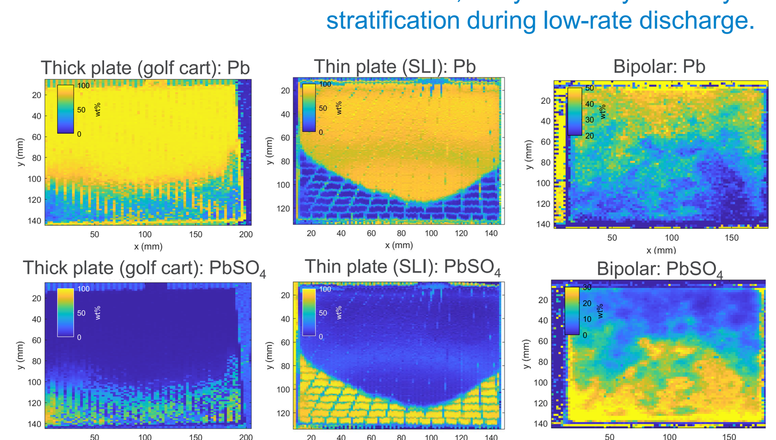


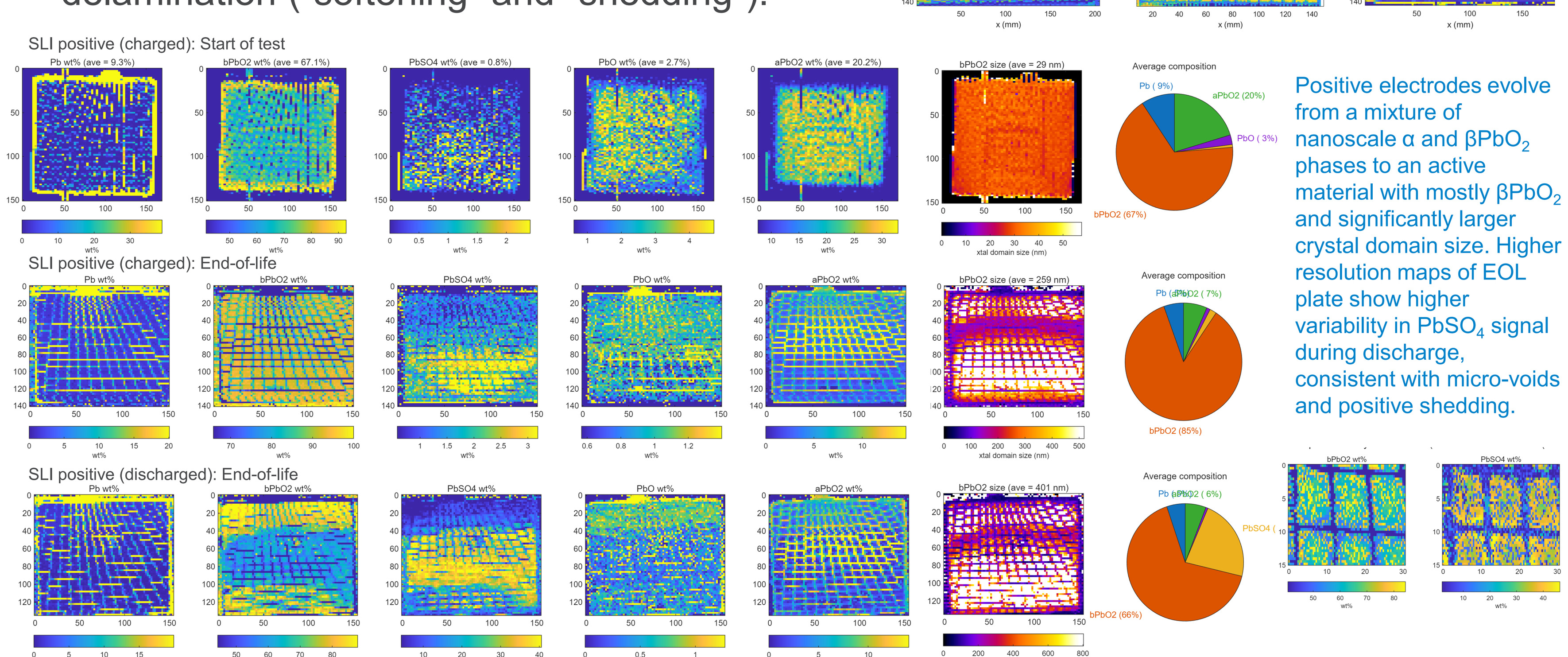
CELL AND ELECTRODE ANALYSIS: HIGH ENERGY XRD

Analysis of over 500 electrodes show two predominant failure mechanisms:

- Negative electrode sulfation/stratification: buildup of inactive $PbSO_4$ at bottom of cells.
- $\alpha \rightarrow \beta PbO_2$ conversion and crystal ripening in positive electrodes that leads to active material delamination ("softening" and "shedding").

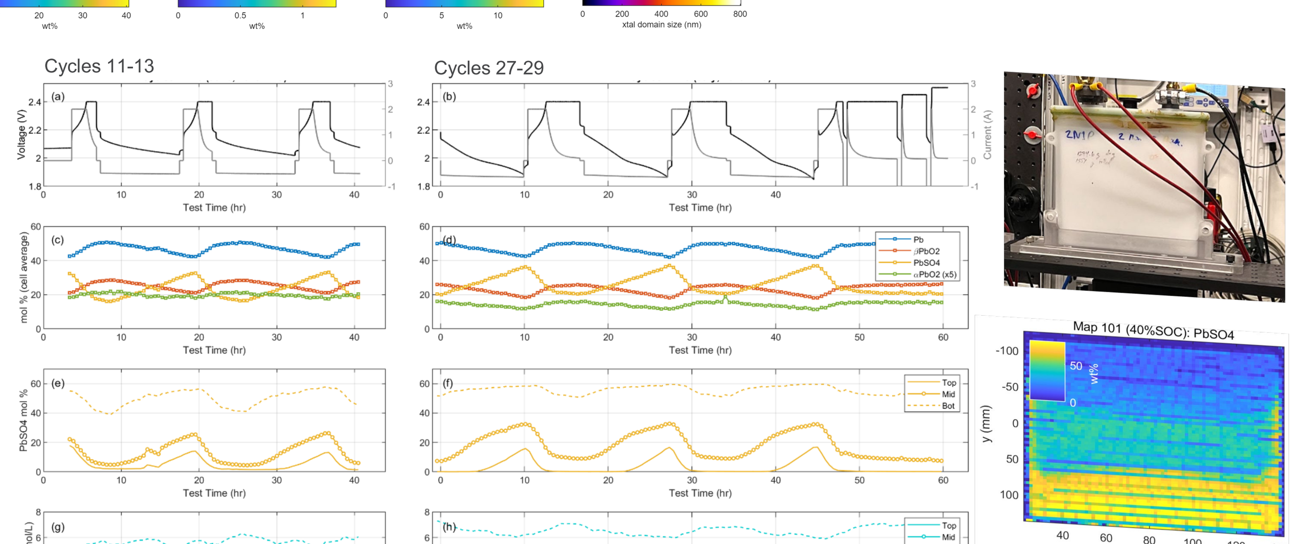
End-of-life negative electrodes frequently exhibit the accumulation of $PbSO_4$ at the bottom of the cell, likely driven by electrolyte stratification during low-rate discharge.





Positive electrodes evolve from a mixture of nanoscale α and βPbO_2 phases to an active material with mostly βPbO_2 and significantly larger crystal domain size. Higher resolution maps of EOL plate show higher variability in $PbSO_4$ signal during discharge, consistent with micro-voids and positive shedding.

Cycling of in situ cells confirms accumulation of $PbSO_4$ at the bottom of the cell, driven by variable acid concentration, which become exacerbated with cycling. Despite these gradients, cells have maintained rated capacity for over a year of cycling.

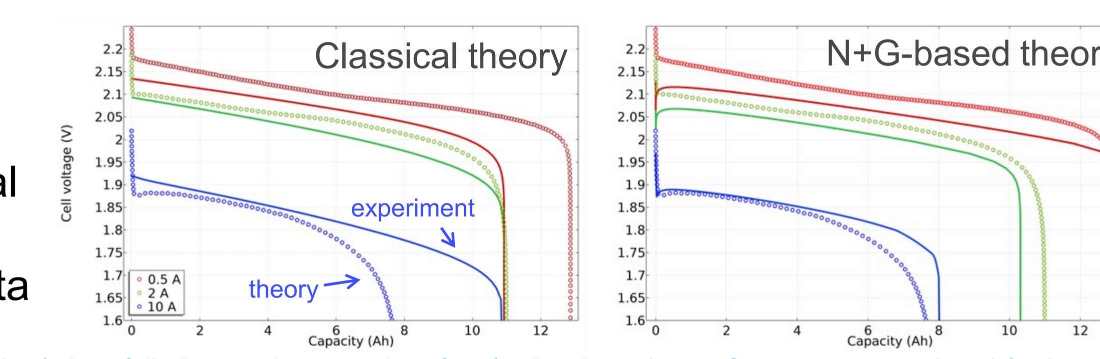


Left: changes in electrode and electrolyte species. Right example of cell and map from XRD refinements.

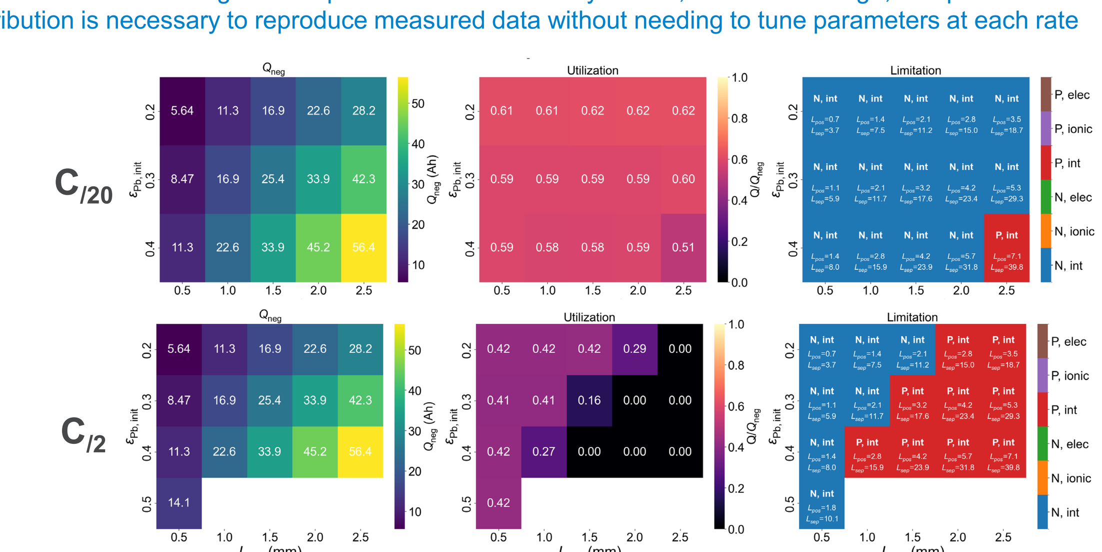
MODELING: LIMITS OF UTILIZATION

A continuum-level electrochemical model has been developed and validated against voltammetry data (flat lead) and negative-limited porous electrode cells. The included physics:

- Faradaic reaction at electrode-electrolyte interface
- Transport of the acid
- Transport of $PbSO_4$
- Nucleation of $PbSO_4$
- Growth of $PbSO_4$
- Change of electrode specific surface area (1/m)
- Change of electrode volume fractions
- Conservation of electronic and ionic charge

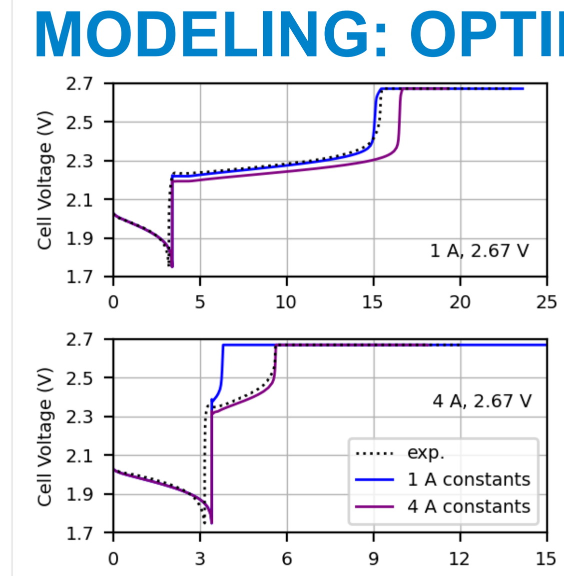


Simulation of discharge – incorporation of nucleation dynamics, surface coverage, and particle size distribution is necessary to reproduce measured data without needing to tune parameters at each rate



This model can help predict utilization over a wide parameter space. Above: example of theoretical utilization with varying porosity (ε), thickness (L) for 20 hr and 2 hr discharge rates ($R_{0,neg}$=0.5μm, acid conc. = 5 M)

MODELING: OPTIMIZING RECHARGE

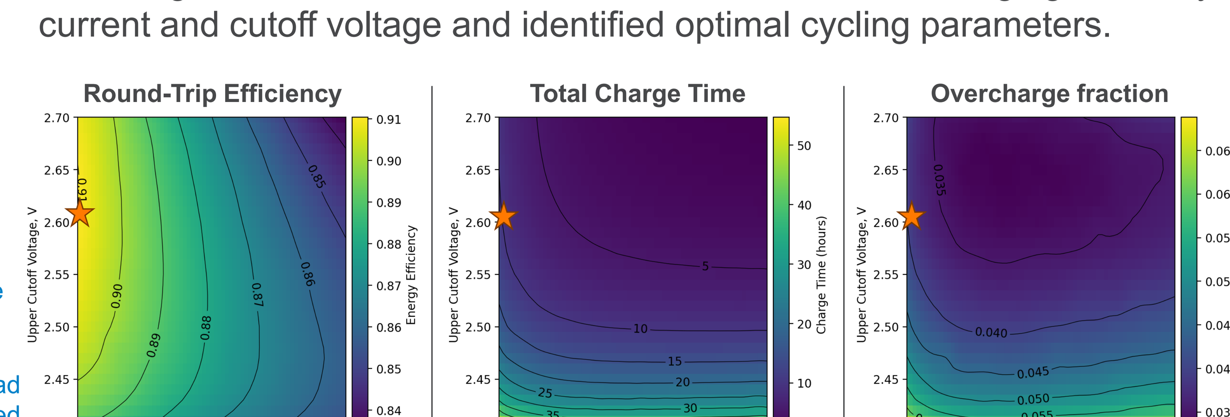


Above: porous electrode model for 1A and 4A recharge compared with flooded three electrode cell data.

Charge model validated against flooded pos-limited cells

- Concentration-dependent diffusivity, conductivity, and OCV
- Previously validated kinetic models (nucleation & growth for discharge, dissolution/deposition for charge)
- Uses 4 A (C/2.5) rate constants for all charging simulations

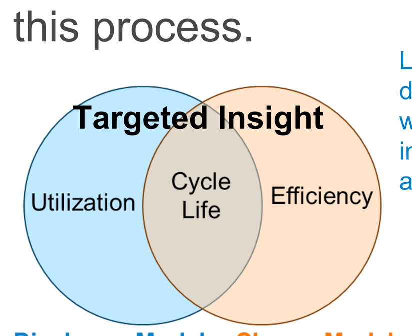
Resulting model was used to simulate 50 → 100%SOC charging with varying current and cutoff voltage and identified optimal cycling parameters.



Right: predicted design space for flooded lead acid batteries. The most efficient recharge used lower currents than current CLBL protocol. Ideal recharge conditions indicated by star.

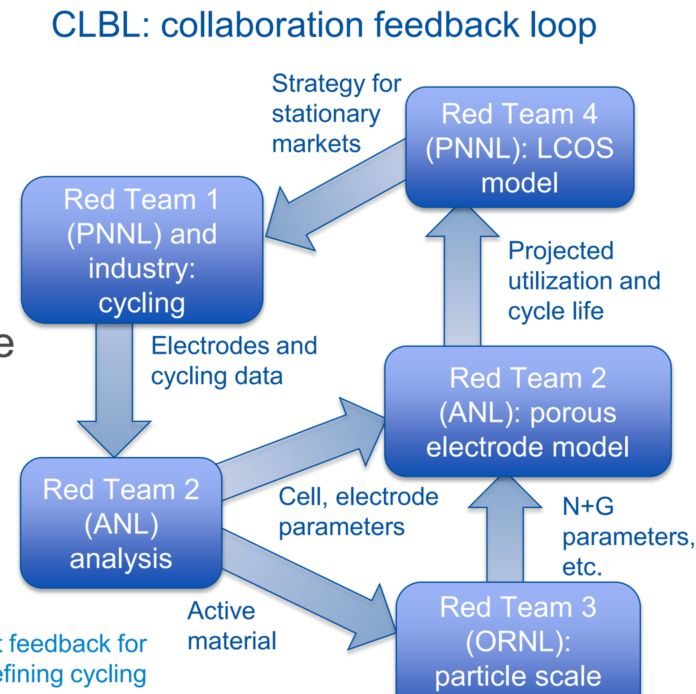
CONCLUSIONS AND IMPACT

- Measurements on industry-provided electrodes from cells using CLBL protocol is largely complete.
- Insights and models into observed failure modes are helping refine cycling parameters and use-cases.
- Models for utilization and recharge will help accelerate this process.



Left: parallel development of discharge and charge models will lead to overall improvements in cost and cycle life for lead acid batteries.

CLBL: collaboration feedback loop



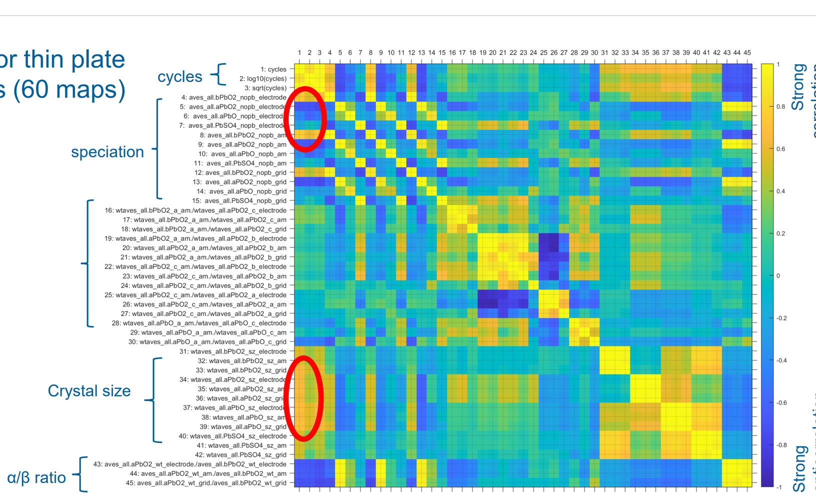
Right: Red Team 2 provides important feedback for industry and Teams 1, 3 and 4 for refining cycling parameters and atomistic models to identify ideal use cases for lead acid in stationary markets.

NEXT STEPS

Characterization: correlation of structural features from XRD analysis to cycling data.

- This framework quantifies correlations between structural features and with cycling parameters.
- Begin collecting microstructural data with Red Team 3.

Right: correlation matrix for thin plate positives (60 maps)



Gantt chart for modeling team

Main Task	FY25				FY26				FY27			
Sub Task	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1D model												
Charge model development												
Discharge model development												
Combined charge/discharge model												
1D model validation (1st ~10 cycles)												
Long-term cycling model												
Determine detail/computational limits												
Develop reduced order model												
Long-term model validation												
Study Design Space												
1D model (1st ~10 cycles)												
Long-term cycling												
Support Red Team #4 TEA												

Modeling: 1D model is nearly complete.

- FY26 and F27 will begin to study evolution of cycling data and electrode parameters during cycling.
- Correlating with 2V cell data and data from industry/PNNL.

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